

SHORT COMMUNICATION

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Revised data for combeite, Na₂Ca₂Si₃O₉. By REINHARD X. FISCHER and EKKEHART TILLMANN, *Mineralogisches Institut der Universität Würzburg, Am Hubland, D-8700 Würzburg, Federal Republic of Germany*

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Abstract

Refinements of the crystal structures of the high- and low-temperature modifications of combeite, previously described by Fischer & Tillmanns [*Neues Jahrb. Mineral. Monatsh.* (1983), pp. 49–59] are revised and compared with synthetic analogues. Both forms of the mineral with approximate composition Na₂Ca₂Si₃O₉ ($Z = 6$) consist of six-rings of SiO₄ tetrahedra which are circular in the high-temperature form [$R\bar{3}m$, $a = 10.429$ (2), $c = 13.149$ (3) Å] and elliptically distorted in the low-temperature form [$P3_121$, $a = 10.464$ (2), $c = 13.176$ (3) Å].

Introduction and results

Recent refinements of the crystal structures of Na₂CaSi₂O₆ (Ohsato, Maki & Takéuchi, 1985) and Na₄Ca₄Si₆O₁₈ (Ohsato, Takéuchi & Maki, 1986) prompt us to publish revised data for the two forms of combeite which are isostructural with the synthetic compounds. Combeite is a mineral with approximate composition Na₂Ca₂Si₃O₉. We solved the structures of both compounds (Fischer, 1983; Fischer & Tillmanns, 1983) and refined them in space group $R\bar{3}m$ (high-temperature form) and $P3_2$ (low-temperature form), respectively. The structural features including the cation distribution (Fischer, 1983) are nearly identical to what has been found and described by Ohsato *et al.* (1985, 1986) for the synthetic analogues, except for the fact that we were not able to refine the low-temperature form in one of the proposed enantiomorphous space groups $P3_121$ or $P3_221$. Ohsato *et al.* (1986) relate this to the fact that we (presumably) did not carry out site-occupancy refinements, which in fact, we did (Fischer, 1983). The solution to the problem is simpler: direct methods for the solution of the crystal structure in $P3_121$ gave a model of the rhombohedral substructure with $R\bar{3}m$ symmetry. All 3₂ axes in the supergroup are symmetrically equivalent and they are intersected by twofold axes, which is not the case in space group $P3_121$, where one set of screw axes is not intersected by twofold axes. Since we did not recognize this ambiguity we chose the wrong origin in space group $P3_121$, and all attempts to refine the model failed unless we reduced the symmetry to $P3_2$. The atomic coordinates of the $P3_2$ structure, however, correspond to $P3_121$ symmetry within a few standard deviations. The results of the new refinement of

the structure in space group $P3_121$ (Table 1) show the close relationship between the mineral and the synthetic compound.

Table 2 contains the results of the refinements for the high-temperature form of combeite. The reinvestigation of the two structures included a constrained refinement of the site occupancies and the results are compared with those given by Fischer (1983) and Ohsato *et al.* (1985, 1986).

Experimental and crystal data

(a) *Low-temperature modification.* Microprobe analysis gave the chemical composition Na_{2.2}Ca_{1.9}Si₃O₉ with traces of Mg and Fe; full-matrix least-squares refinement in $P3_121$ with constraints on site occupancies to yield the total composition as given by the microprobe analysis; $a = 10.464$ (2), $c = 13.176$ (3) Å, 1566 unique reflections with $I > 2\sigma(I)$, $R = 0.050$, $wR = 0.047$, $w = 1.4/[\sigma^2(F) + 10^{-3}F^2]$; $Z = 6$; variable parameters = 155, max. shift/ $\sigma = 0.03$, mean shift/ $\sigma = 0.008$; the highest peak in the difference Fourier map was at 0.30, 0, 0.64 with approximately $2 e \text{ \AA}^{-3}$, which is close to the split position $M1'$ (Table 1) given by Ohsato *et al.* (1986), but a site-occupancy refinement of sodium on this position gave only approximately 0.3Na/unit cell, and therefore it has not been included in the final refinements. Si–O distances range from 1.562 (5) (Si2–O6) to 1.650 (5) Å (Si2–O4) with mean values of 1.614 (4), 1.611 (5) and 1.614 (4) Å for the three symmetrically independent SiO₄ tetrahedra.

(b) *High-temperature form.* Microprobe analysis Na_{2.4}Ca_{1.5}(Fe,Mn,Mg,Zn)_{0.3}Si₃O₉, refinement in $R\bar{3}m$ with constraints on site-occupancy factors to give a total of 9 Ca/unit cell and assigning the rest to sodium assuming fully occupied $M1$, $M3$ and $M4$ sites as indicated in preliminary unconstrained refinements (Fischer, 1983); $a = 10.429$ (2), $c = 13.149$ (3) Å; 372 unique reflections with $I > 2\sigma(I)$, $R = 0.042$, $wR = 0.039$, $w = 4.8/[\sigma^2(F) + 5 \times 10^{-6}F^2]$; $Z = 6$; variable parameters = 41, max. shift/ $\sigma = 0.005$, mean shift/ $\sigma < 0.001$; highest peak in difference Fourier map close to $M4$ with approximately $1.3 e \text{ \AA}^{-3}$. A second peak with approximately $1.1 e \text{ \AA}^{-3}$ at 0.16, 0, 0.5 is about 1 Å away from O1 and not comparable with the split position (Table 2) given by Ohsato *et al.* (1985). Si–O distances range from 1.584 (4) to 1.625 (4) Å with a mean value of 1.605 (4) Å.

Table 1. Positional parameters in fractional coordinates, equivalent isotropic displacement factors and occupancies for the low-temperature form compared with the respective values given by Ohsato *et al.* (1986) for the low-temperature form of the synthetic compound

Standard deviations are given in parentheses after the last significant digit. First and second line refer to this work and to Ohsato *et al.* (1986) respectively.

$$U_{eq} = (\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j) / 3.$$

	x	y	z	$U_{eq}(\text{\AA}^2)$	Site symmetry and position*	d^\dagger	Atoms/unit cell	
							Na	Ca
Si1	0.1978 (3)	0.1523 (3)	0.7759 (1)	0.007 (1)	1 6c	0.06		
	0.1986 (1)	0.1526 (1)	0.7780 (1)	0.006 (1)				
Si2	0.4973 (3)	0.3207 (2)	0.8958 (1)	0.007 (1)	1 6c	0.07		
	0.4996 (1)	0.3234 (1)	0.8958 (1)	0.007 (1)				
Si3	0.6269 (2)	0.1489 (3)	0.7643 (1)	0.007 (1)	1 6c	0.06		
	0.6243 (1)	0.1485 (1)	0.7635 (1)	0.006 (1)				
O1	0.1616 (8)	0	$\frac{1}{2}$	0.028 (5)	.2. 3b	0.09		
	0.1671 (3)	0		0.018 (1)				
O2	0.5591 (9)	0	$\frac{1}{2}$	0.028 (5)	.2. 3b	0.07		
	0.5555 (3)	0		0.020 (1)				
O3	0.3445 (5)	0.2787 (6)	0.8354 (4)	0.017 (3)	1 6c	0.05		
	0.3442 (2)	0.2842 (2)	0.8382 (1)	0.011 (1)				
O4	0.5861 (6)	0.2639 (7)	0.8217 (4)	0.021 (3)	1 6c	0.06		
	0.5849 (2)	0.2643 (2)	0.8199 (2)	0.013 (1)				
O5	0.2439 (6)	0.1479 (6)	0.6611 (4)	0.016 (3)	1 6c	0.09		
	0.2468 (2)	0.1535 (2)	0.6622 (1)	0.014 (1)				
O6	0.4683 (8)	0.2435 (5)	0.0015 (4)	0.023 (3)	1 6c	0.09		
	0.4782 (2)	0.2472 (2)	0.0032 (1)	0.015 (1)				
O7	0.5547 (5)	0.1109 (8)	0.6552 (3)	0.019 (2)	1 6c	0.07		
	0.5513 (2)	0.1104 (3)	0.6540 (1)	0.017 (1)				
O8	0.0688 (5)	0.1892 (5)	0.7922 (4)	0.013 (3)	1 6c	0.07		
	0.0652 (2)	0.1853 (2)	0.7949 (1)	0.010 (1)				
O9	0.5939 (6)	0.4961 (5)	0.8881 (4)	0.018 (3)	1 6c	0.05		
	0.5965 (3)	0.4991 (2)	0.8880 (1)	0.017 (1)				
O10	0.8011 (5)	0.2184 (6)	0.7774 (4)	0.016 (3)	1 6c	0.05		
	0.7990 (2)	0.2184 (2)	0.7763 (1)	0.014 (1)				
M1	0.3125 (2)	0.9845 (2)	0.5889 (1)	0.016 (1)	1 6c	0.04	3.1 (6)	2.6 (4)
	0.3086 (1)	0.9830 (1)	0.5892 (1)	0.007 (1)			1.77 (6)	1.23 (6)
M1'	—	—	—	—	1 6c	—	—	—
M21	0.2821 (7)	0.9704 (5)	0.6151 (5)	0.033 (3)	1 6c	0.15	1.77 (6)	1.23 (6)
	0.5032 (6)	0.3366 (4)	0.6644 (2)	0.023 (1)			6.0	—
M22	0.5041 (2)	0.3380 (2)	0.6642 (1)	0.021 (1)	.2. 3a	0.22	6.0	—
	0.8115 (19)	0	$\frac{1}{2}$	0.049 (10)			1.2 (1)	—
M31	0.5196 (3)	0.3618 (3)	0.1579 (2)	0.023 (2)	1 6c	0.07	2.9 (6)	2.8 (4)
	0.5262 (1)	0.3704 (1)	0.1558 (1)	0.020 (1)			2.46 (6)	3.54 (6)
M32	0.8217 (3)	0	$\frac{1}{2}$	0.010 (1)	.2. 3b	0.08	—	3.0
	0.8203 (1)	0		0.010 (1)			—	3.0
M4	0.3083 (2)	0	$\frac{1}{2}$	0.007 (1)	.2. 3a	0.08	—	3.0
	0.3039 (1)	0		0.007 (1)			—	3.0
Total, this work							13.2	11.4
Total, Ohsato <i>et al.</i> (1986)							12.0	12.0

* After *International Tables for Crystallography* (1983).

† Offset (\AA) from twofold symmetry for the atoms given by Fischer (1983) in $P3_1$.

Table 2. Parameters for the high-temperature form (explanations as in heading to Table 1); second line of atom list refers to Ohsato *et al.* (1985)

	x	y	z	$U_{eq}(\text{\AA}^2)$	Site symmetry and position	Atoms/unit cell	
						Na	Ca†
Si1	0.1511 (1)	—x	0.5642 (1)	0.014 (1)	.m 18h		
	0.1502 (1)	—x	0.5636 (1)	0.007 (1)			
O1	0.2511 (5)	0	$\frac{1}{2}$	0.050 (2)	.2 18g		
	0.2533 (6)	0.0131 (6)		0.5147 (3)			
O2	0.1150 (2)	—x	0.6740 (3)	0.034 (2)	.m 18h		
	0.1161 (1)	—x	0.6734 (2)	0.034 (1)			
O3	0.2385 (2)	—x	0.5548 (3)	0.038 (2)	.m 18h		
	0.2373 (1)	—x	0.5510 (2)	0.033 (1)			
M1	0	0	0.2505 (2)	0.019 (1)	3m 6c	3.6 (1)	2.4 (1)
	0	0	0.2485 (1)	0.013 (1)			
M2	$\frac{1}{2}$	0	0	0.028 (2)	.2/m 9e	6.8 (1)	—
	$\frac{1}{2}$	0	0	0.034 (2)			
M3	$\frac{1}{2}$	0	$\frac{1}{2}$	0.023 (1)	.2/m 9d	5.4 (1)	3.6 (1)
	$\frac{1}{2}$	0		0.017 (1)			
M4	0	0	0	0.012 (1)	3m 3a	—	3.0
	0	0	0	0.010 (1)			
Total, this work						15.8	9.0
Total, Ohsato <i>et al.</i> (1985)						17.49	9.26

* Statistically occupied by 18 oxygen atoms.

† In our refinements constrained to give $M1(\text{Ca}) + M3(\text{Ca}) = 6$, assuming full occupation of $M1$, $M3$ and $M4$.

All computer programs used in this work are referenced by Fischer & Tillmanns (1983):*

Discussion

Fischer & Tillmanns (1983) did point out the disturbing fact that the structure of the low-temperature form had no twofold axis in $xx0$ although the diffraction pattern clearly indicated Laue class $3m$ and not $\bar{3}$. However, they did not draw the right conclusion. Many cases of unnecessarily low symmetry in crystal-structure determinations are known in the literature, and a number of ways to avoid such errors have been given by Baur & Tillmanns (1986). The present case belongs to Baur & Tillmanns' category (2) cases, which are quoted as most difficult to identify because of the lack of a special method for recognizing them. We could probably have avoided our error if we had relied on the clear evidence for higher Laue symmetry in the diffraction pattern, which after all is the physical basis for the determination and refinement of crystal structures.

Because of uncertainties in the distribution of the 1.8 (Fe, Mn, Mg, Zn) atoms in the unit cell of the high-temperature form the total of sodium and calcium could not be constrained properly in the refinements, thus giving rise to a

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44025 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

false value of 15.8 Na/unit cell while 14.4 Na/unit cell are expected from the microprobe analysis. The refinement was based on the assumption that the cation sites $M1$, $M3$ and $M4$ are fully occupied as indicated in unconstrained refinements. The results are similar to what has been found by Ohsato *et al.* (1985, 1986). However, our refinements of the low-temperature form clearly showed the presence of scattering matter in site $M22$, which is vacant in the refinements of Ohsato *et al.* (1985). So far the phase transition has not been structurally investigated by *in situ* experiments. The crystals investigated by us and by Ohsato *et al.* (1985, 1986) have different compositions in the high- and low-temperature forms, thus not giving sufficient information on the phase transition of the unique compound. *In situ* experiments are in progress to give additional information on the phase transition in the solid-solution series.

References

- BAUR, W. H. & TILLMANNS, E. (1986). *Acta Cryst.* B42, 95–111.
 FISCHER, R. X. (1983). Thesis, Univ. Mainz, Federal Republic of Germany.
 FISCHER, R. X. & TILLMANNS, E. (1983). *Neues Jahrb. Mineral. Monatsh.* pp. 49–59.
International Tables for Crystallography (1983). Vol. A, pp. 501, 535. Dordrecht: Reidel.
 OHSATO, H., MAKI, I. & TAKÉUCHI, Y. (1985). *Acta Cryst.* C41, 1575–1577.
 OHSATO, H., TAKÉUCHI, Y. & MAKI, I. (1986). *Acta Cryst.* C42, 934–937.

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